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### Computational Analysis of Liquid Crystalline Biphenylcyclohexane Derivatives: Estimation of Configurational Entropy, and Phase Stability

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# Computational Analysis of Liquid Crystalline Biphenylcyclohexane Derivatives: Estimation of Configurational Entropy, and Phase Stability

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*A comparative computational analysis of two liquid crystalline disubstituted biphenylcyclohexanes (BCHs) of general formula  $R-C_6H_{10}-C_6H_4-X$  with  $R: C_3H_7$ ;  $X: H$  (BCH30), and  $R: C_5H_{11}$ ;  $X: CN$  (BCH5CN) has been carried out on the basis of quantum mechanics, statistical mechanics, and intermolecular forces. The atomic net charge and dipole moment at each atomic center have been evaluated using the complete neglect differential overlap (CNDO/2) method. The modified Rayleigh–Schrodinger perturbation theory, along with multicentered–multipole expansion method, has been employed to evaluate the long-range intermolecular interactions, while a “6-exp” potential function has been assumed for short-range interactions. The interaction energy values obtained through these computations have been taken as input to estimate the configurational entropy and Helmholtz free energy at room temperature, transition temperature, and above transition temperature. The present investigation provides valuable information in understanding the flexibility of a particular configuration at different temperatures. Further, it serves as a molecular model to yield the structure-phase stability relationship.*

**Keywords** CNDO/2 method; configurational entropy; interaction energy; phase stability

## Introduction

Liquid crystals fill the symmetry gap between the highest-symmetry homogenous isotropic fluid phase and the lowest-symmetry crystalline lattice [1]. The field of liquid crystals has been paid much scientific attention, as some level of disorderness is present in any naturally occurring thermodynamic system. This attention can be partly ascribed to many successful and technological applications, and has significantly benefited from the impact of computational techniques [2, 3]. These studies will provide systematic structure property information through which links can be established between molecular properties and the microscopic interactions between them. Their results served as a test system for many experimental measurements on liquid crystal systems [4]. Structural correlations of different molecules with different chemical constituents/physical properties can be studied at molecular level providing information about intermolecular interactions [5–7].

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The property of ordering in the liquid crystalline phase arises from the presence of anisotropic intermolecular forces. Important examples of these include short-range repulsive forces and long-range dispersion, and electrostatic and polarization interactions. Among these, the short-range interactions, coupled with the high degree of shape anisotropy typical for most nematogens, is generally believed to be the principal factor underlying the stability of the phase [8, 9]. The long-range interactions, which arise from the presence of permanent molecular electrostatic multipole moments, are believed to have a smaller effect on molecular ordering. An important objective in the study of liquid crystals is the attempt to gain a detailed understanding of the effects of each of the components of the intermolecular pair potential on the phase structure and its stability [10].

The role of molecular interactions in mesomorphic compounds has engrossed the attention of several workers [11–15] based on the Rayleigh–Schrodinger perturbation method. These studies were aimed at establishing the anisotropic nature of the pair potential, and subsequently finding out the minimum energy configuration of a pair of liquid crystalline molecules. Thus, the main emphasis was laid on finding out the minimum energy with observed crystal structure, the basic motive for ordering of a molecule. It has been observed that the interaction energies for a pair of mesogens indicate the preference of a particular configuration over the other depending on their energy values. These values, however, do not replicate the actual relative preference, which can only obtain through their relative energies corresponding to each configuration. Further, significant differences among the energies of various configurations are noticed, in terms of multipole interactions, which must have a marked effect on thermodynamic properties of the system. Hence, these relative energies are used as an input to calculate the thermodynamic properties of BCH30 and BCH5CN molecules.

The present work aims at estimating the configurational entropy [16] of BCH30 and BCH5CN molecules to analyze the structurally distinct configurations during the phase transition phenomenon. The relative energies between a molecular pair of BCH30 and BCH5CN have been computed at an intermediate distance of 6 Å for stacking and 8 Å for in-plane interactions. Similarly, a distance of 22 Å has been kept for terminal interactions. The choice of distance has been made to eliminate the possibility of van der Waals contacts completely and to keep the molecule within the short- and medium-range interactions. Further, Helmholtz free energy values have also been computed to elucidate [16] the thermodynamic stability of the mesophases. An examination of thermodynamic data has revealed that BCH30 exhibits smectic B-isotropic transition temperature at 366 K [17] and BCH5CN exhibits nematic–isotropic transition temperature at 494 K [17].

## Computational Technique

The molecular geometry of BCH30 and BCH5CN has been constructed on the basis of the published crystallographic data with the standard values of bond lengths and bond angles. In both the compounds, the molecules form layers in the crystalline state. The dihedral angles between the phenyl rings in the biphenyl unit are 23.8° (BCH30) and 2.4° (BCH5CN), respectively [17]. A number of following methodologies have been carried out in this work.

### *Computation of Atomic Net Charge and Dipole Moments*

In order to calculate the interaction energy between a molecular pair, it is necessary to compute atomic net charges and dipole moments through an all-valence electron method.

Hence, in the present work, the CNDO/2 method [18] has been used to compute the net atomic charges and dipole moments at each atomic center of the molecule because using only the Mulliken atomic net charges (given, for example, by an *ab initio* program) for the calculation of an electrostatic interaction would be incorrect for two reasons: (1) the atomic dipoles must be taken into account, and (2) the homopolar dipoles must be taken into account, or else atomic net charges obtained according to Lowdin's procedure should be used. An *ab initio* program, which gives only Mulliken net charges is, therefore, quite misleading as concerns a reasonable representation of the molecular charge distribution in terms of charges and dipoles [19].

### Computation of Interaction Energy at Various Configurations

A detailed computational scheme based on simplified formula provided by Claverie [20] for evaluating the interaction energy of a molecular pair has been used to calculate the energy at fixed configurations. According to the second order of the perturbation theory, as modified for intermediate range interactions [21], the total pair interaction energy of molecules ( $U_{\text{pair}}$ ) is represented as a sum of several terms contributing to the total energy:

$$U_{\text{pair}} = U_{\text{el}} + U_{\text{pol}} + U_{\text{disp}} + U_{\text{rep}},$$

where  $U_{\text{el}}$ ,  $U_{\text{pol}}$ ,  $U_{\text{disp}}$ , and  $U_{\text{rep}}$  are the electrostatic, polarization, dispersion, and repulsion energy terms, respectively.

Further, electrostatic term is expressed as

$$U_{\text{el}} = U_{\text{QQ}} + U_{\text{QMI}} + U_{\text{MIMI}} + \dots,$$

where  $U_{\text{QQ}}$ ,  $U_{\text{QMI}}$ ,  $U_{\text{MIMI}}$ , etc., are monopole–monopole, monopole–dipole, and dipole–dipole terms, respectively. In fact, the inclusion of higher order multipoles does not affect significantly the electrostatic interaction energy and the calculation only up to the dipole–dipole term gives the satisfactory results [11–15, 22]. The computation of electrostatic term has, therefore, been restricted only up to dipole–dipole energy term.

In the present work, the dispersion and short-range repulsion terms are considered together because several semiempirical approach, viz., the Lennard-Jones or Buckingham-type approaches, actually proceed in this way. Kitaygorodsky introduced a Buckingham formula whose parameters were later modified by Kitaygorodsky and Mirskaya for hydrocarbon molecules and several other molecules, and finally give the expression [23]:

$$U_{\text{disp}} + U_{\text{rep}} = \sum_{\lambda}^{(1)} \sum_{\nu}^{(2)} U(\lambda, \nu),$$

$$U(\lambda, \nu) = K_{\lambda} K_{\nu} (-A/Z^6 + B e^{-\gamma Z}),$$

where  $Z = R_{\lambda\nu}/R_{\lambda\nu}^0$ ;  $R_{\lambda\nu}^0 = [(2R_{\lambda}^w)(2R_{\nu}^w)]^{1/2}$ , where  $R_{\lambda}^w$  and  $R_{\nu}^w$  are the van der Waals radii of  $\lambda$  and  $\nu$  atoms, respectively. The parameters  $A$ ,  $B$ , and  $\gamma$  do not depend on the atomic species. But  $R_{\lambda\nu}^0$  and factor  $K_{\lambda} K_{\nu}$  allow the energy minimum to have different values according to the atomic species involved. The necessary formulae may be found elsewhere [24].

The origin has been chosen on an atom close to the center of mass of the molecule. The x-axis has been directed along a bond parallel to the long molecular axis, while y-axis lies in the plane of the molecule, and the z-axis is normal to the molecular plane (x–y).

### Computation of Thermodynamic Parameters

The total interaction energy values obtained through these computations have been used as input to calculate the following thermodynamic parameters [16] of a particular configuration  $i$  in order to obtain a better insight into phase stability and configurational entropy of selected mesogens:

$$A = -kT \ln \sum_i \exp(-\beta \varepsilon_i)$$

$$S = k \ln \sum_i \exp(-\beta \varepsilon_i) + (U/T)$$

$$U = \sum_i \varepsilon_i \exp(-\beta \varepsilon_i) / \sum_i \exp(-\beta \varepsilon_i),$$

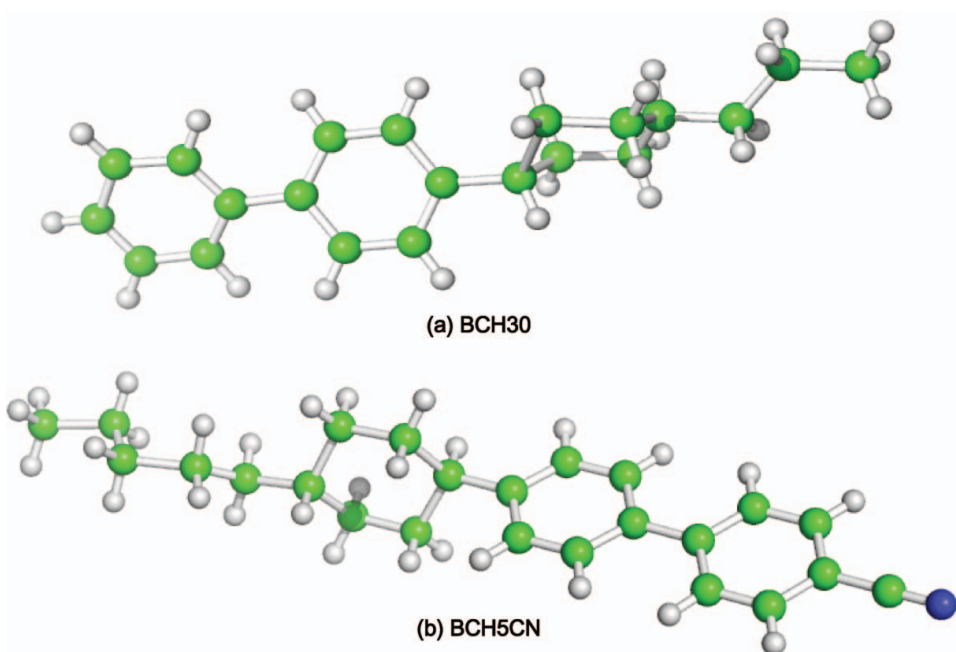
where  $A$  stands for Helmholtz free energy,  $S$  stands for entropy.  $\beta = 1/kT$ ,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature.  $U$  is the internal energy of the system and  $\varepsilon_i$  represents the energy of the configuration  $i$  to the minimum energy value.

### Results and Discussion

The molecular geometry of BCH30 and BCH5CN is shown in Fig. 1. The study of molecular charge distribution and the results of interaction energy calculations during the different modes of interactions are discussed below.

#### Molecular Charge Distribution and Phase Stability

The electrostatic interactions between a pair of molecules represent a significant contribution to the total pair energy. It is expected that the specific charge distributions and



**Figure 1.** Molecular geometry of BCH30 and BCH5CN.

**Table 1.** CNDO/2 group charges and transition temperatures for BCHs molecules

Molecule	Side group	Core	Alkyl	Temperature (K) [17]
BCH30	0.005	0.058	−0.064	366
BCH5CN	−0.082	−0.015	0.098	494

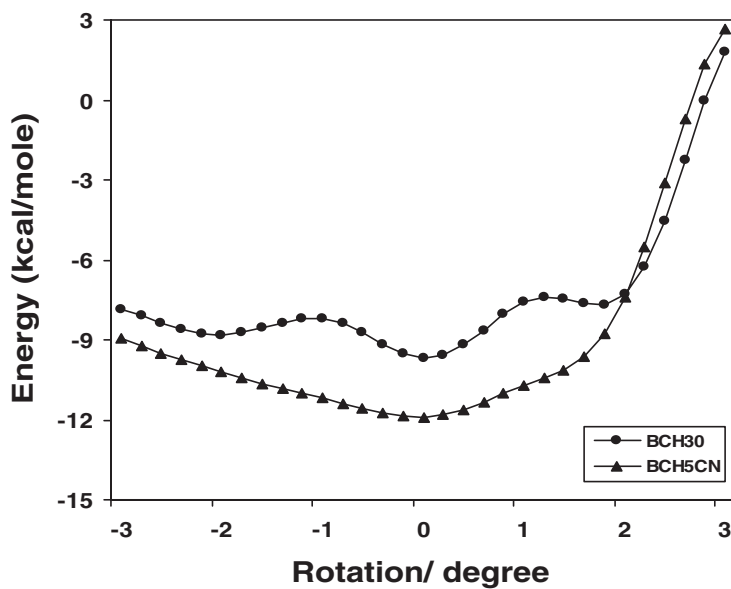
electrostatic interactions in LC molecules play a decisive role in the formation of various mesophases. Analysis of molecular charge distribution can deliver good information about local electrostatic interactions, which is not possible from an experimental point of view. To parameterize the molecular interactions for computational studies, atom-positioned partial charges are helpful. The atomic charges, which describe the intermolecular potential, are generally assumed to be conformationally independent. Quantum chemical computations offer the possibility of taking a detailed look at the electronic structure and phase stability of the molecules. This can be achieved by determining atom-based partial charges, which are not quantum mechanical observables.

The group charges were calculated for both molecules (Table 1) in order to explain the phase stability of the systems. It is evident from Table 1 that the negatively charged alkyl chains in the BCH30 molecule will be strongly attracted by the positively charged core as well as side group (H). However, the positively charged alkyl chains in the BCH5CN molecule will have a strong attraction due to the high negative charge present on the core as well as the cyano group. This causes the formation of longer units in the mesophase. Hence, the phase stability is expected to be high for BCH5CN. The transition temperatures ( $T_{N-I}$ ,  $T_{S-I}$ ) of the molecules reported by the crystallographer are in agreement with this finding (Table 1).

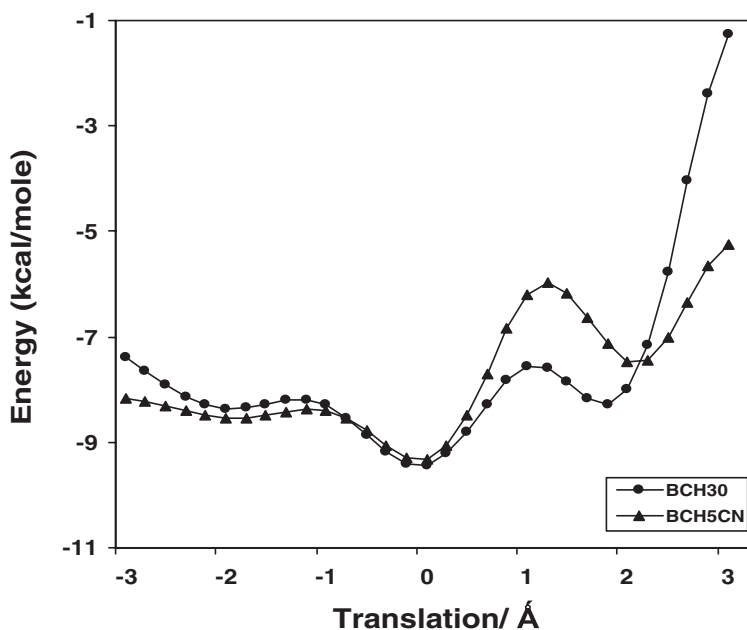
### Stacking Interactions

One of the interacting molecules has been fixed in the x–y plane such that the x-axis lies along a bond parallel to the long molecular axis, while the other has been kept at a separation of 6 Å along the z-axis with respect to the fixed one. The variation of total interaction energy component with respect to rotation about x-axis corresponding to the configuration y (0°) z (0°) is shown in Fig. 2 for BCH30 and BCH5CN molecules. It has been observed that the main attractive part of the energy comes through the dispersion term. It is due to the fact that the face-to-face orientation molecular rings produce larger attractive dispersion energy, although the exact minimum is estimated always from Kitaygorodsky energy curve, which has gross similarity with the total energy curve. The variation of interaction energy with respect to translation along x-axis corresponding to the configuration y (0°) z (180°) is shown in Fig. 3 for BCH30 and BCH5CN molecules. The variation of energy is almost constant in the region of  $-1.8 \pm 0.6$  Å, which shows a sliding of one molecule over other is energetically allowed for a small range that may be correlated with the fluidity of the compound maintaining its alignment in the mesophase.

The variation of interaction energy components with respect to rotation about the z-axis corresponding to configuration x (0°) z (0°) has also been carried out for BCH30 and BCH5CN molecules. It has been observed that the configuration shows a sharp preference toward the minimum energy point. The minimum energy thus obtained has been taken as the starting point, and the entire process has been repeated for small intervals. The energy



**Figure 2.** Variation of stacking interaction energy with respect to rotation about x-axis corresponding to the configuration y (0°) z (0°) for BCH30 and BCH5CN.



**Figure 3.** Variation of stacking interaction energy with respect to translation along x-axis corresponding to the configuration y (0°) z (180°) for BCH30 and BCH5CN.

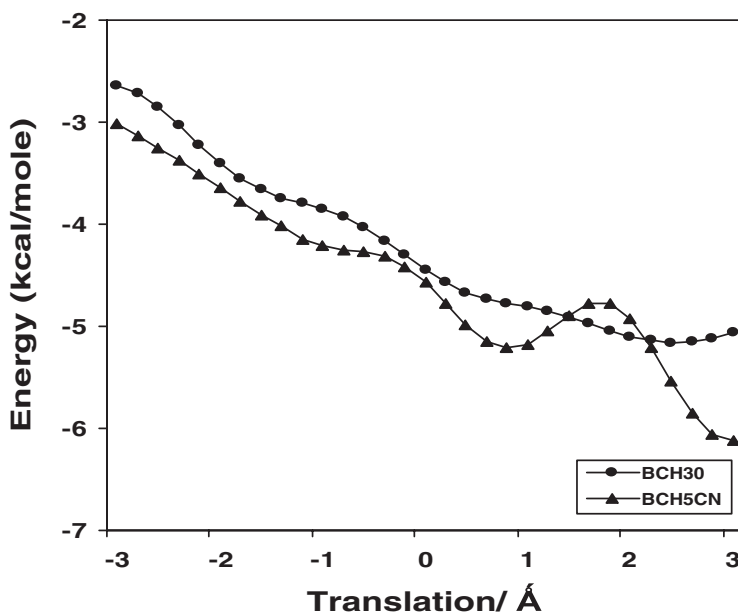
has been minimized with respect to translations and rotations about the x, y, and z axes. An accuracy of 0.1 Å in translation and 1° in rotation of one molecule with respect to other has been achieved. It is important to note here that the path of minimization strictly depends on the objective of computations. The global search for minimum energy configuration or the study of variation of interaction energy under preselected condition will have completely different path and, therefore, one has to be careful in choosing the specific route.

### *In-plane Interactions*

An interacting molecule has been kept at a distance of 8 Å along the y-axis with respect to the fixed one in order to avoid the possibility of van der Waals contacts completely. The similar calculations have been performed for in-plane interactions. Again, rotations about y- and x-axis have been given and the corresponding energy has been minimized with respect to translation and rotation about all axes.

The variation of interaction energy components with respect to rotation about the x-axis corresponding to configuration y (0°) has been carried for both the molecules, and it is observed that the main attractive part of the energy comes through dispersion term. The observed in-plane interactions are more pronounced than the stacking interactions.

Further, the variation of total interaction energy components with respect to translation along x-axis corresponding to configuration y (0°) is shown in Fig. 4 for BCH30 and BCH5CN molecules. It has been observed that electrostatic energy during in-plane interactions is more effective than stacking, since the antiparallel orientation of molecular rings provides more effective dipole–dipole attractions. Additionally, repulsive



**Figure 4.** Variation of in-plane interaction energy with respect to translation along x-axis corresponding to the configuration y (0°) for BCH30 and BCH5CN.



quadrupole–quadrupole interactions become less effective due to the slipped antiparallel molecular ring orientation. The total interaction energy is nearly constant in the range of  $-0.8 \pm 0.4$  Å, which may be correlated with the fluidity of the compound maintaining its alignment in mesophase.

### ***Terminal Interactions***

To investigate terminal interactions, the interacting molecule has been shifted along x-axis by 22 Å with respect to fixed one. It has been observed that the terminal interactions are much weaker than stacking or in-plane interactions (after due consideration of short contact). The variation of total interaction energy components with respect to rotation about x-axis corresponding to configuration y ( $0^0$ ) has been carried out for BCH30 and BCH5CN molecules. It has been observed that rotations about the x-axis show absolutely no preference for any angle, i.e., the molecules are completely free to rotate about their long molecular axis. However, for rotations about y-axis, it has been observed that there is slight preference for the molecular axis being on the same line.

### **Role of Molecular Interactions**

The configurational entropy and Helmholtz free energy of BCH30 and BCH5CN molecules have been estimated with respect to translation along the long molecular axis to analyze the role of molecular interactions on phase stability/behavior of BCHs molecules.

### ***Phase Stability***

The present computations are helpful to correlate the phase stability/behavior of the compounds as well as to understand the role of molecular motions, interactions, and disordering of alkyl chains in a particular phase. Estimation of Helmholtz free energy provides better understanding of ordering and phase stability at molecular level. A comparative picture of Helmholtz free energy with respect to translation along x-axis during the stacking and in-plane interactions of BCH30 and BCH5CN molecules at room temperature, transition temperature, and above transition temperature is given in Table 2. Evidently, the Helmholtz free energy of BCH30 during stacking interactions is  $-1.09$  kcal/mol at room temperature (300 K) that decreased to  $-1.47$  kcal/mol at smectic B-isotropic transition temperature (366 K). The Helmholtz free energy of BCH5CN molecule during the stacking interactions is  $-1.05$  kcal/mol at room temperature (300 K) that decreased to  $-2.27$  kcal/mol at nematic–isotropic transition temperature (494 K). The increment in negative free energy confirms stability of the mesophase at transition temperature. Moreover, the large free energy difference from transition temperature to room temperature reveals that the phase stability is high for BCH5CN (Table 2). This is in agreement with the molecular charge distribution analysis.

### ***Estimation of Configurational Entropy***

The terminal flexible chains reduce the stability of solid crystal phase, and allow the appearance of liquid crystal phases. From the view point of entropy, alkyl chains play a dominant role as they are very labile, and can easily make multi conformational changes

**Table 2.** A comparative picture of Helmholtz free energy ( $A$ ) corresponding to various configurations during stacking and in-plane interactions at room temperature (300 K), transition temperature (\*), and above transition temperature (\*\*\*) of BCH30 and BCH5CN molecules with respect to translation along x-axis

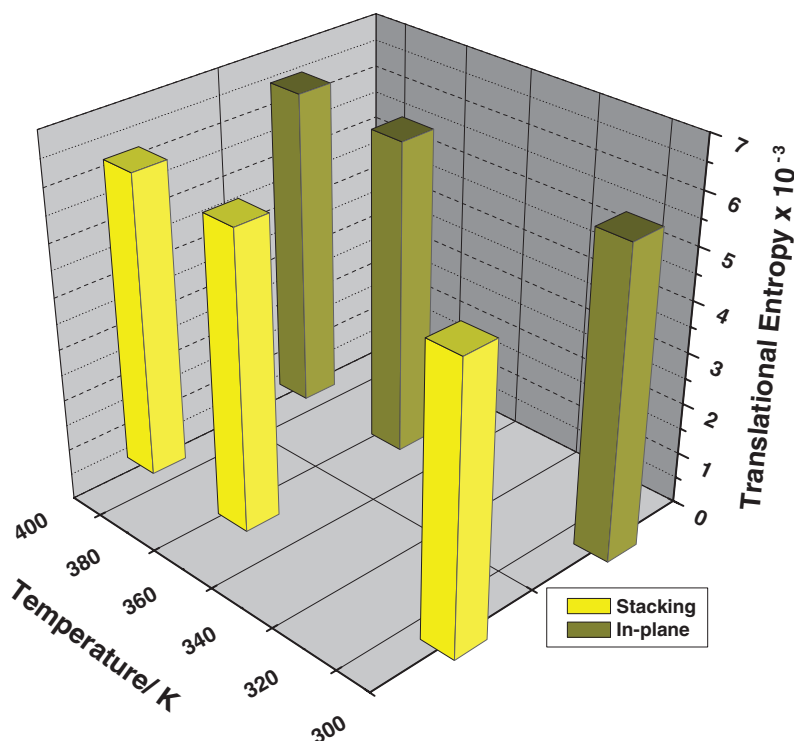
Molecule	Configuration	Temperature (K)	Helmholtz free energy (kcal mol <sup>-1</sup> )
BCH30	y (0 <sup>0</sup> ) z (180 <sup>0</sup> ) <sup>a</sup>	300	-1.09
		366*	-1.47
		400**	-1.67
	y (0 <sup>0</sup> ) <sup>b</sup>	300	-1.50
		366*	-1.90
		400**	-2.12
BCH5CN	y (0 <sup>0</sup> ) z (180 <sup>0</sup> ) <sup>a</sup>	300	-1.05
		494*	-2.27
		550**	-2.62
	y (0 <sup>0</sup> )	300	-0.96
		494*	-2.10
		550**	-2.45

<sup>a</sup>Stacking interactions.

<sup>b</sup>In-plane interactions.

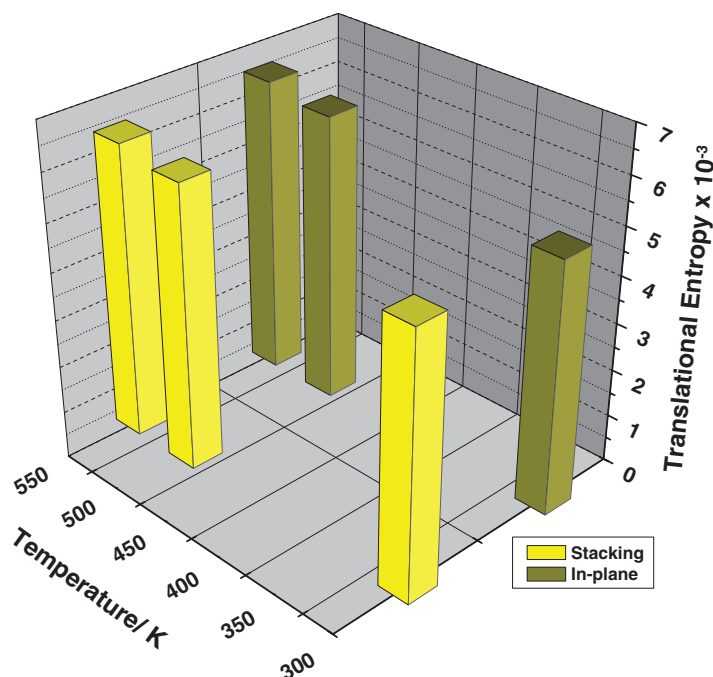
Hence, alkyl chains can be regarded as source of entropy to realize a given condensed state or to tune the delicate balance between two energetically close phases.

The configurational entropy has been estimated with respect to translational motion during the stacking and in-plane interactions for BCH30 and BCH5CN molecules. Hence, the configurational entropy can be regarded as translational entropy. The variation of translational entropy for BCHs molecules at room temperature, transition temperature, and above transition temperature along the long molecular axis is shown in Figs. 5 and 6, respectively. Evidently, the translational entropy during stacking interactions is  $5.8 \times 10^{-3}$  kcal mol<sup>-1</sup> k<sup>-1</sup> at smectic B-isotropic transition temperature (366 K). However, at room temperature (300 K), the value is  $5.5 \times 10^{-3}$  kcal mol<sup>-1</sup> k<sup>-1</sup> for BCH30 molecule. Further, the translational entropy for BCH5CN during stacking interactions is  $6.05 \times 10^{-3}$  kcal mol<sup>-1</sup> k<sup>-1</sup> at nematic-isotropic transition temperature (494 K). However, at room temperature (300 K), the value  $5.5 \times 10^{-3}$  kcal mol<sup>-1</sup> k<sup>-1</sup> indicates a strong binding at low temperature with less disorder. But with the increase in temperature, the molecules obtain sufficient freedom to slide along the long molecular axis, which causes the increment of disorder. Hence, a large entropy difference from transition temperature to room temperature has been observed for BCH5CN. A less entropy difference of BCH30 molecule indicates that the molecule prefers a stacked layered structure, which justifies the smectic character. The similar calculations during in-plane interactions suggest that BCH5CN molecule exhibits more translational freedom. These results favor the nematic character of BCH5CN molecule. Further, the comparable values of configurational entropy during the both modes of interactions (i.e., stacking and in-plane) suggests that BCH30 molecule has higher ordering along z-axis (stacking) and BCH5CN has higher ordering along y-axis (in-plane), which subsequently confirms the smectic and nematic behaviors of the molecules.



**Figure 5.** Variation of translational entropy (unit: kcal mol<sup>-1</sup> K<sup>-1</sup>) during stacking and in-plane interactions at room temperature (300 K), smectic–isotropic transition temperature (366 K), and above transition temperature (400 K) for BCH30.

It may be noted that though the freedom is considerable for smaller translation, longer translations are not generally permitted. Thus, in the mesomorphic range, small movements of molecule are only possible. Most of the liquid crystalline molecules found to have a number of conformations, which are thermally accessible. In the process of a phase transition from a low- to a high- temperature, the molecular motions of the alkyl chains would be excited and thereby the number of thermally accessible conformations would be increased. The translational entropy in the isotropic liquid states is increased from its room temperature for each molecule (Figs. 5 and 6). It implies that the different modes of molecular motions (translational, rotational, etc.) are excited to an equal extent, particularly in the isotropic state. Translational entropy favors parallel alignment of the molecules because this arrangement gives less excluded volume (the volume into which the center of mass of one molecule cannot move due to the impenetrability of the other molecule) and, therefore, more free space for the molecules to jostle around. Moreover, the parallel arrangement represents a state of low orientational entropy. This has been observed for biphenyl cyclohexane derivative (BCH) molecules during the rotational motion. However, the comparable values in both cases (i.e., stacking and in-plane interactions) show that BCH30 molecules prefer in forming the stacked layered structure, justifies the smectic character. BCH5CN molecule does not show extraordinary preference in forming the stacked layered structure, hence justifies the nematic character.



**Figure 6.** Variation of translational entropy (unit: kcal mol<sup>-1</sup> K<sup>-1</sup>) during stacking and in-plane interactions at room temperature (300 K), nematic–isotropic transition temperature (494 K), and above transition temperature (550 K) for BCH5CN.

## Conclusions

The computational analysis of liquid crystalline biphenyl cyclohexane derivatives (BCHs) leads to the following conclusions:

- (1) The group charge analysis of BCH molecules reveals that the phase stability is expected to be high for BCH5CN molecule. Further, the large free energy difference for BCH5CN from transition temperature to room temperature also confirms the high thermodynamic stability of mesophase.
- (2) The flexible end chains of molecules provide enough configurational entropy to prevent the total crystallization of the core and expanding the stability of mesophase range.
- (3) Translational entropy shows the flexibility of a particular configuration in each phase that has a direct relation with the phase transition property. Further, the analysis of different molecular motions (translational, rotational) and interactions (stacking, in-plane, etc.) are helpful to analyze the phase behavior/stability of mesophases.

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